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Transition Metal Cluster Complexes: Part III—Antiferromagnetic Spin Coupling in Cu(II) & Ni(II) Complexes with Diacetylazinedioxime

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Diacetylazinedioxime complexes of Cu(II) and Ni(II) halides, of the types, Cu_2LX_4 (X = Cl or Br) and $Ni_2L_2X_4$ (X = Cl, Br or I) have been prepared and characterized on the basis of analytical, IR and electronic spectral and magnetic moment data. IR spectral data show that diacetylazinedioxime acts as a bi = bidentate ligand coordinating through the azine and oxime nitrogens. Cu(II) complexes may have planar structures with two copper atoms bound in edge-on position to a single molecule of the ligand. The Ni(II) complexes are suggested to possess a hydrogen bonded binuclear structure on the basis of IR data. Electronic spectra reveal a tetragonal crystal field around nickel (II) ions. The magnetic susceptibility values, over a range of temperature, show a marked decrease of moments with decreasing temperature indicating the presence of antiferromagnetic spin-coupling in these Complexes. The moments calculated on the basis of Heisenberg-Dirac-Van Vleck model agree well with the experimental results. The mutual interaction apparently takes place through π-electron system of the bridging conjugated ligand.

BINUCLEAR metal complexes of azines and related ligands have generated considerable interest in recent years[1-8]. The ligands are expected to be planar due to high degree of conjugation and coordination with metal ions is restricted to the plane along the edge of the ligand. In an earlier communication, we have reported the inner type of complexes of diacetylazinedioxime ($DAADOH_2$) with Cu(II) and Ni(II)[6]. Magnetic susceptibility values over a range of temperatures show the presence of antiferromagnetic exchange-coupling in these systems. The present paper deals with the isolation of a new series of complexes with Cu(II) and Ni(II) halides, where the uncharged ligand acts in a tetrafunctional manner coordinating to two metal ions. Magnetic susceptibilities of the complexes have been studied from ambient to 80°K and the data treated on the basis of Heisenberg-Dirac-Van Vleck model.

Materials and Methods

All the chemicals used were BDH or E. Merck samples.

The ligand ($DAADOH_2$) was prepared as reported earlier[6]; m.p. 220° (lit. m.p. 220°).

Tetrachlorodiacetylazinedioxime dicopper (II) — Diacetylazinedioxime (0·49 g) was dissolved in ~ 30 ml absolute ethanol. $CuCl_2.2H_2O$ (0·9 g) dissolved in ~ 20 ml of absolute ethanol was added to the ligand solution. A bright green precipitate was readily formed which was filtered, washed with ethanol and dried *in vacuo* [Found: Cu, 26·98, Cl, 29·78. Calc. for $Cu_2(DAADOH_2)\ Cl_4$: Cu, 27·04; Cl, 30·49%].

Tetrabromodiacetylazinedioxime dicopper (II) — It was prepared in a similar manner using ethanolic solution of Cu(II) bromide [Found: Cu, 19·64; Br, 49·50. Calc. for $Cu_2(DAADOH_2)\ Br_4$: Cu, 19·56; Br, 49·60%].

Tetrachlorobis(diacetylazinedioxime) dinickel (II) — Diacetylazinedioxime (0·5 g) was dissolved in ~130 ml ethanol. $NiCl_2.6H_2O$ dissolved in ~30 ml of ethanol was added to the above solution. The mixture was refluxed for an hour over a hot water-bath when an yellowish product appeared. It was filtered, washed with acetone and dried. [Found: Ni, 17·91; Cl, 20·98; N, 16·76. Calc. for $Ni_2(DAADOH_2)_2\ Cl_4$: Ni, 18·00; Cl, 21·70; N, 17·07%].

Tetrabromobis(diacetylazinidioxime) dinickel (II) — It was synthesized in a similar manner as the chloride complex using an ethanolic solution of Ni(II) bromide [Found: Ni, 14·04; Br, 38·00; N, 13·01. Calc. for $Ni_2(DAADOH_2)_2Br_4$: Ni, 14·10; Br, 38·30; N, 13·40%].

Tetraiodobis(diacetylazinedioxime) dinickel (II) — Starting with a ethanolic solution of Ni(II) iodide, the iodide complex was prepared in a similar manner as the chloride complex [Found: Ni, 11·40; I, 48·69; N, 10·54. Calc. for $Ni_2(DAADOH_2)_2I_4$: Ni, 11·50; I, 49·70; N, 10·50%].

All the physical measurements were carried out as reported earlier[6].

Results and Discussion

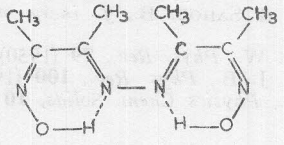
Analytical results show that the Cu(II) complexes have the stoichiometry, Cu_2LX_4 (X = Cl or Br) and the Ni(II) complexes $Ni_2L_2X_4$ (X = Cl, Br or I). The complexes are soluble in water and several polar solvents such as ethanol, methyl cyanide and dimethyl sulphoxide.

The IR spectrum of the ligand (I) shows strong and broad bands near 3300 and 3220 cm^{-1} indicating strong inter- or intra-molecular hydrogen bonding involving N-OH groups. In the spectra of the

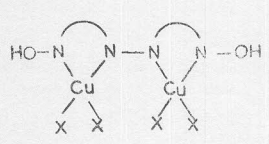
Cu(II) complexes relatively sharp bands are observed in this region but in the case of Ni(II) complexes, the bands are broad indicating the existence of hydrogen bonding in the latter series of complexes. Band due to N-OH deformation persists in the complexes and occurs in the region 1700-1650 cm^{-1} further confirming the presence of O-H groups and the existence of the ligand in its unionized form. Both the νC=N bands due to the azine and oxime groups, shift to higher frequencies in the metal complexes indicating coordination through nitrogen atoms of these groups. The shift is due to metal to ligand π-electron interaction.

A band appearing in the region 1085-1050 cm^{-1} in the spectra of the present complexes has been assigned to N-O stretching. Thus, keeping in view the analytical and IR data, the Cu(II) complexes have been assigned the structure (II) in which a ligand molecule coordinates in a bi-bidentate manner to two Cu(II) ions, with four chloride or bromide ions completing the coordination spheres of the copper ions. On the other hand, Ni(II) complexes are suggested to have a binuclear hydrogen bonded macrocyclic structure (III) with halide ions coordinating to complete the tetragonally distorted octahedral structure. However, polymetallic structures having out-of-plane interactions can not be ruled out.

The Cu(II) complexes show an asymmetric broad band at 19000 cm^{-1} and an intense charge-transfer band at 23000 cm^{-1} in their electronic spectra.

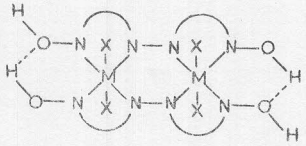


(I)



X = Cl or Br

(II)



X = Cl, Br or I

(III)

The broad ligand-field band represents two or three superimposed absorptions and leads us to believe that the present tetracoordinated Cu(II) complexes are essentially planar.

The electronic spectral data of Ni(II) complexes are recorded in Table 1. These show the characteristic features of the Ni(II) ion in a tetragonal field with *trans* nitrogen atoms and acido groups occupying axial positions. *d-d*-Transitions are observed in the region 12000-18000 cm^{-1} (extinction coefficient ~30) followed by a strong charge-transfer band. The spectra have been compared with the spectra of several known Ni(II) complexes with the chromophores NiN_4O_2 and are found to be similar.

The experimental magnetic susceptibilities (Tables 2 and 3) were corrected for diamagnetism and temperature independent paramagnetism (loc cit). Values for J, the exchange integral, and g the Lande splitting factor were derived employing Eq. 1 given by Bleany and Bowers.

$$\chi'_m = \frac{Ng^2\beta^2}{3kT}\,\frac{6\exp(J/kT)}{1+3\exp(J/kT)} + N_\alpha \qquad \ldots(1)$$

The J value for $Cu_2(DAADOH_2)Cl_4$ is found to be negative (~ -59 cm^{-1}) which suggests that antiferromagnetic interaction takes place within a complex unit; the magnetic exchange interaction between copper atoms taking place through the intervening ligand atoms.

In the case of Ni(II) complexes, the μ_{eff} values at room temperature lie within the range expected for octahedrally coordinated Ni(II) with a $^3A_{2g}$ ($t_{2g}^6 e_g^2$) ground state. As the temperature is lowered, μ_{eff} values gradually decrease and attain a value

Table 2 — Magnetic Susceptibility Data of $Cu_2(DAADOH_2)Cl_4$

($J = -59 \pm 2{\cdot}0$ cm^{-1}, $g = 2{\cdot}10$)

Temp. (°K)	$\chi'_A \times 10^{-6}$ (e.m.u.)	μ_{eff} (B.M.)	Temp. (°K)	$\chi'_A \times 10^{-6}$ (e.m.u.)	μ_{eff} (B.M.)
304·5	1199·5	1·71	184·0	1895·7	1·65
295·0	1237·0	1·71	160·0	1107·5	1·60
275·5	1316·8	1·70	136·5	2259·0	1·57
252·5	1445·4	1·70	125·5	2330·7	1·53
233·5	1558·9	1·69	—	—	—

$N_\alpha = 60 \times 10^{-6}$ (e.m.u.)

Table 1 — Electronic Spectral Data of Ni(II) Complexes

(Molar extinction coefficient ~30)

Compound	Solvent	$^3B_{1g} \rightarrow {}^3B_{2g}$	$^3B_{1g} \rightarrow {}^3A_{2g}$	$^3B_{1g} \rightarrow {}^3E_g$
$Ni_2(DAADOH_2)_2Cl_4$	Ethanol	13500	—	15400
	DMSO	13500	14100	15600 17300
$Ni_2(DAADOH_2)_2Br_4$	CH_3CN	13700	—	16400 (broad)
	DMSO	13500	14300	Overlapped by CT band
$Ni_2(DAADOH_2)_2I_4$	Ethanol	—	15400	17900

TABLE 3 — MAGNETIC SUSCEPTIBILITY DATA OF Ni(II) COMPLEXES

Temp. (°K)	$\chi'_A \times 10^{-6}$ (e.m.u.)	μ_{eff} (B.M.)	Temp. (°K)	$\chi'_A \times 10^{-6}$ (e.m.u.)	μ_{eff} (B.M.)
$Ni_2(DAADOH_2)_2Cl_4$ [$J = -12 \pm 1{\cdot}0$ cm^{-1}, $g = 2{\cdot}2$]					
295·0	3995	3·07	193·0	6176	3·08
285·0	4177	3·09	167·0	6895	3·07
268·0	4486	3·09	147·0	7686	3·01
249·0	4817	3·09	128·0	8667	2·98
234·0	5090	3·08	97·0	10029	2·75
222·0	5679	3·17	89·0	10871	2·78
$Ni_2(DAADOH_2)_2Br_4$ [$J = -18 \pm 2{\cdot}0$ cm^{-1}, $g = 2{\cdot}0$]					
304·0	4007	3·11	196·0	5945	3·08
295·0	4074	3·09	164·0	6598	2·94
281·0	4362	3·12	140·0	7472	2·88
277·0	4278	3·08	109·0	8755	2·76
239·0	5073	3·10	93·0	9203	2·62
228·0	5412	3·11	89·0	9443	2·59
$Ni_2(DAADOH_2)_2I_4$ [$J = -0 \pm 2{\cdot}0$ cm^{-1}, $g = 2{\cdot}05$]					
305·5	3050	2·73	216·5	4346	2·70
295·0	3109	2·70	184·0	5103	2·70
286·0	3237	2·72	143·0	6198	2·65
275·5	3377	2·72	111·30	7236	2·53
262·5	3493	2·70	89·0	8193	2·42
241·5	3832	2·72	78·0	8706	2·31

$N\alpha = 200 \times 10^{-6}$ (e.m.u.).

between 2·3 and 2·7 B.M. at about 80°K. The comparison of the experimental results with the susceptibility values theoretically calculated using Eq. 2 for a dimeric complex of nickel indicates that there is antiferromagnetic intracluster interaction (negative J).

$$\chi'_A = -\frac{Ng^2\beta^2}{kT}\,\frac{1+5\exp(4J/kT)}{3+5\exp(4J/kT)+\exp(-2J/kT)} + N_\alpha \quad \ldots(2)$$

The essential requirement for antiferromagnetic coupling between Ni(II) ions is the availability of suitable overlapping orbitals of proper symmetry[12-14]. In our opinion the significant pathway for the exchange coupling between Ni(II) ions is via the π-electron system of the conjugated diacetylazine-dioxime group which functions as the bridge between metal centres.

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